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合8年10月17日專利死因修正本

POLYMERS OF CARBON MONOXIDE WITH MONO-OLEFINS

Novel copolymers of carbon monoxide with one or more optionally alkyl-substituted cyclopentenes, are obtainable by contacting the monomers with a catalyst composition solution comprising: (a) a palladium compound, (b) an anion of an acid with a pKa of less than 2, and (c) a bidentate ligand containing phosphorus, sulphur or nitrogen, with the proviso that when a bidentate ligand chosen from nitrogen, sulphur or aromatic phosphorus containing compounds is used as component (c), the catalyst composition additionally comprises a meta-dinitrobenzene compound as component (d).

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The invention relates to novel polymers of carbon monoxide with one or more mono-olefins.

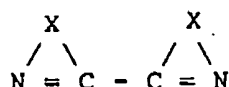
It is known that linear polymers of carbon monoxide with one or more alpha-olefins, in which the units originating in carbon monoxide on the one hand, and the units originating in the applied alpha-olefins on the other hand, occur in alternating order, can be prepared by contacting the monomers with a catalyst composition on the basis of

- a) a palladium compound,
- b) an anion of an acid with a pKa of less than 2, and
- c) a phosphorus, sulphur or nitrogen bidentate ligand, which bidentate ligand meets certain structural requirements.

Eligible phosphorus bidentate ligands are compounds of the general formula $(R^1)_2P-R-P(R^1)_2$, wherein R^1 is an optionally polar-substituted aromatic hydrocarbyl group and R is a bivalent organic bridging group containing at least two carbon atoms in the bridge. Examples of such phosphorus bidentate ligands are 2,2-dimethyl-1,3-bis(diphenylphosphino)propane and 1,3-bis[bis(2-methoxyphenyl)phosphino]propane.

Eligible sulphur bidentate ligands are compounds of the general formula $R^2S-R-SR^2$, in which R^2 is an optionally polar-substituted hydrocarbyl group and R has the meaning given hereinbefore. Examples of such sulphur bidentate ligands are 1,2-bis(ethylthio)ethane and cis-1,2-bis(benzylthio)ethene.

Eligible nitrogen bidentate ligands are compounds of the general formula



wherein X is an organic bridging group containing three or four atoms in the bridge at least two of which are carbon atoms. Examples of such nitrogen bidentate ligands are 2,2'-bipyridine and 1,10-phenanthroline.

5 The afore-mentioned catalyst compositions are excellently suitable both for preparing linear alternating copolymers of carbon monoxide with a single alpha-olefin, such as ethene, propene, butene-1 or octene-1 and for preparing linear terpolymers of carbon
10 monoxide with two alpha-olefins, such as ethene and propene or ethene and octene-1. By taking up certain organic oxidants in the afore-mentioned catalyst compositions, their polymerizing activity can be considerably enhanced. Examples of organic oxidants
15 that are suitable for the purpose are 1,4-benzoquinone, 1,4-naphthoquinone, nitrobenzene, para-chloronitrobenzene and ortho-dinitrobenzene.

The Applicant has carried out an investigation into whether the afore-mentioned catalyst compositions
20 can be considered for use in the preparation of linear alternating polymers of carbon monoxide with cyclopentene and/or with one or more cyclopentenenes which carry an alkyl substituent in the 3, 4 and/or 5
position. The investigation has shown that the
25 afore-mentioned catalyst compositions as such cannot be used for this purpose. Neither the catalyst compositions containing a phosphorus bidentate ligand nor those containing a sulphur or nitrogen bidentate ligand did produce any appreciable degree of
30 polymerization. This situation could not be improved by incorporating the afore-mentioned polymerization promoters.

Further investigation carried out by the Applicant into this subject has now surprisingly shown that the afore-mentioned catalyst compositions can be made suited to the preparation of linear alternating
5 polymers of carbon monoxide with one or more cyclopentenes which are optionally alkyl-substituted in the 3, 4 and/or 5 position, by introducing a modification in their compositions.

Both for the catalyst compositions containing a
10 phosphorus bidentate ligand of the general formula $(R^1)_2P-R-P(R^1)_2$ and for the catalyst compositions containing a sulphur or a nitrogen bidentate ligand it was found that to this end, a compound should be taken up in the catalyst compositions as component d) in
15 which there occurs a benzene ring substituted with at least two nitro groups in a meta position relative to one another. For the catalyst compositions containing a phosphorus bidentate ligand of the general formula $(R^1)_2P-R-P(R^1)_2$ it was further found that the desired
20 object can also be attained by replacing the bidentate ligand with a phosphorus bidentate ligand of the general formula $(R^3)_2P-R-P(R^3)_2$, wherein R^3 represents an optionally polar-substituted aliphatic hydrocarbyl group and R has the meaning given hereinbefore.

25 On the basis of the configurations of the asymmetrical carbon atoms present in the polymer chains, the linear alternating copolymers of carbon monoxide with cyclopentenes can be divided into stereo-regular and stereo-irregular copolymers. If the
30 configuration of the asymmetrical carbon atoms in the polymer chains is random, the copolymers are referred to as stereo-irregular. If this configuration is substantially regular, the copolymers are referred to as stereo-regular. The latter copolymers are obtained
35 when during the copolymerization of carbon monoxide

with cyclopentene, use is made of a catalyst composition containing a phosphorus bidentate ligand of the general formula $(R^3)_2P-R-P(R^3)_2$.

5 Linear alternating polymers of carbon monoxide with one or more cyclopentenes which are optionally alkyl-substituted in the 3, 4 and/or 5 position are novel. Naturally, this also holds for the stereo-regular carbon monoxide/cyclopentene copolymers.

10 The present patent application therefore relates to novel polymers of carbon monoxide with one or more mono-olefins, which polymers can be defined as follows

- a) they can be prepared by polymerizing carbon monoxide with one or more cyclopentenes which are optionally alkyl-substituted in the 3, 4 and/or 5 positions,
 - 15 b) they have a linear structure, and
 - c) in the polymers, the units originating in carbon monoxide on the one hand, and the units originating in the applied cyclopentenes on the other hand, occur in alternating order.
- 20

The patent application further relates to processes for the preparation of these polymers.

If the polymers of the invention are based on alkyl-substituted cyclopentenes, the alkyl groups present therein preferably do not contain more than 4 carbon atoms. An example of a suitable dialkylcyclopentene is 3,5-dimethylcyclopentene. When the polymers are based on alkyl-substituted cyclopentenes, preference is further given to cyclopentenes which contain only one alkyl group, such as 3-methylcyclopentene. Further, there is a preference for polymers of carbon monoxide with only a single optionally alkyl-substituted cyclopentene. Special preference is given to copolymers of carbon monoxide with cyclopentene.

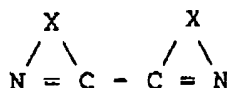
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The polymers of the invention may be prepared by contacting the monomers with a solution of a catalyst composition in a diluent, which catalyst composition is based upon:

- 5 a) a palladium compound,
- b) an anion of an acid with a pKa of less than 2, and
- c) either (1) a phosphorus bidentate ligand of the general formula $(R^3)_2P-R-P(R^3)_2$, or
 (2) a phosphorus bidentate ligand of the general
 10 formula $(R^1)_2P-R-P(R^1)_2$, or
 (3) a sulphur bidentate ligand of the general formula $R^2S-R-SR^2$, or
 (4) a nitrogen bidentate ligand of the general formula



- 15 with the proviso that when a bidentate ligand chosen from the groups (2)-(4) is used as component c), the catalyst composition should in addition include as component d) a compound which has a benzene ring substituted with at least two
 20 nitro groups in a mutual meta position.

- The preparation of the polymers of the invention is preferably carried out at a temperature of from 20 to 120 °C, an overall pressure of from 5 to 150 bar and by employing such a quantity of catalyst composition as
 25 to contain 10^{-7} to 10^{-3} mol of palladium per mol of cycloolefin to be polymerized. Special preference is given to a preparation carried out at a temperature in the range of from 30 to 100 °C, an overall pressure in the range of from 20 to 100 bar and by employing such a
 30 quantity of catalyst composition as to contain 10^{-6} to 10^{-4} mol of palladium per mol of cycloolefin to be polymerized. The molar ratio of the cycloolefins relative to carbon monoxide in the mixture to be

polymerized is preferably from 10:1 to 1:10 and in particular from 5:1 to 1:5. Very suitable diluents are lower aliphatic alcohols, such as methanol and mixtures thereof with cyclic ethers, such as tetrahydrofuran.

5 The palladium compound employed in the catalyst compositions as component a) is preferably a palladium salt of a carboxylic acid, and palladium acetate in particular. Examples of suitable acids with a pKa of less than 2 (determined in aqueous solution at 18 °C)
10 are mineral acids, such as perchloric acid, sulphonic acids, such as para-toluenesulphonic acid, and halogen carboxylic acids, such as trifluoroacetic acid. In the catalyst compositions, component b) may be taken up in the form of an acid and/or in the form of a salt. A
15 very suitable acid is para-toluenesulphonic acid and a very suitable salt is nickel perchlorate. Preferably, the quantity of component b) present in the catalyst compositions is from 0.5 to 100 and in particular from 1 to 50 mol per mol of palladium.

20 If the polymers of the invention are prepared by using a catalyst composition containing as component c) a phosphorus bidentate ligand of the general formula $(R^1)_2P-R-P(R^1)_2$ or $(R^3)_2P-R-P(R^3)_2$, preference is given to compounds in which the optionally polar-substituted
25 hydrocarbyl groups R^1 and R^3 do not contain more than 10 carbon atoms and in particular to compounds in which R^3 is an alkyl group or in which R^1 is a phenyl group which is optionally substituted with an alkoxy group in a position ortho to the phosphorus atom, such as an
30 ortho-methoxyphenyl group. As regards the bridging group R present in the phosphorus bidentate ligands, preference is given to bridging groups containing three atoms in the bridge at least two of which are carbon atoms. Examples of suitable bridging groups R are the
35 $-CH_2-CH_2-CH_2-$ group, the $-CH_2-C(CH_3)_2-CH_2-$ group and

the $-\text{CH}_2-\text{Si}(\text{CH}_3)_2-\text{CH}_2-$ group. Compounds that can be very suitably used as components c) in the present catalyst compositions are

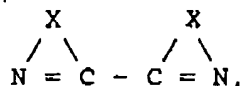
1,3-bis(diphenylphosphino)propane,

5 1,3-bis[bis(2-methoxyphenyl)phosphino]propane, and

1,3-bis(di-n-butylphosphino)propane.

If the polymers of the invention are prepared by using a catalyst composition containing as component c) a sulphur bidentate ligand of the general formula
 10 $\text{R}^2\text{S}-\text{R}-\text{SR}^3$, preference is given to compounds in which the bridging group R contains only two carbon atoms in the bridge. A compound that is very suitable for use as component c) in the present catalyst compositions is 1,2-bis(ethylthio)ethane.

15 If the polymers of the invention are prepared by using a catalyst composition containing as component c) a nitrogen bidentate ligand of the general formula



preference is given to 2,2'-bipyridine and 1,10-phenanthroline.

20 The quantity of component c) present in the catalyst composition is preferably 0.5-100 and in particular 0.75-50 mol per mol of palladium.

If in the preparation of the polymers of the invention it is desired to use a catalyst composition
 25 containing as component c) a bidentate ligand chosen from one of the groups (2)-(4) mentioned earlier, then the catalyst composition should in addition include as component d) a compound which has a benzene ring substituted with at least two nitro groups in a mutual
 30 meta position. Very favourable results have been obtained with 1,3-dinitrobenzene, 2,4-dinitrotoluene and 2,6-dinitrotoluene as the component d).

If the polymers of the invention are prepared by using a catalyst composition containing as component c) a phosphorus bidentate ligand chosen from the afore-mentioned group (1), then it is preferred to incorporate an organic oxidant as component d) for use as a polymerization promoter. Examples of organic oxidants suitable for the purpose are 1,4-benzoquinone, 1,4-naphthoquinone, nitrobenzene, para-chloronitrobenzene and ortho-dinitrobenzene. Any one of the meta-dinitrobenzene compounds mentioned hereinbefore may also be used for the purpose, if desired. If the polymers of the invention are prepared by using a catalyst composition containing as component c) a phosphorus bidentate ligand chosen from the afore-mentioned group (1), then it is preferred to use 1,4-benzoquinone or 1,4-naphthoquinone as component d).

The quantity of component d) present in the catalyst composition is preferably 1-1000 and in particular 5-500 mol per mol of palladium.

The invention will now be illustrated with the aid of the following examples.

Example 1

A carbon monoxide/cyclopentene copolymer was prepared as follows. A stirred autoclave with a capacity of 300 ml and containing 115 ml of tetrahydrofuran and 50 ml of cyclopentene was charged with a catalyst solution which comprised 10 mmol methanol, 0.061 ml palladium acetate, 0.308 mmol nickel perchlorate, 0.074 mmol 1,3-bis(di-n-butylphosphino)propane, and 3.16 mmol 1,4-naphthoquinone.

After carbon monoxide had been blown in until a pressure of 40 bar was reached, the contents of the

autoclave were brought to a temperature of 40 °C. Polymerization was terminated after 60 hours by cooling to room temperature and releasing the pressure. The reaction mixture was stirred into methanol and the
5 copolymer was filtered off, washed with methanol and dried at 50 °C.

7.0 g of copolymer was obtained. The polymerization rate was 9.8 g copolymer/g palladium.hour.

10 Example 2

A carbon monoxide/cyclopentene copolymer was prepared substantially in the same way as in Example 1, except for the following differences

- 15 a) the autoclave contained 115 ml of methanol instead of 115 ml of tetrahydrofuran and
b) the reaction time was 20 instead of 60 hours.

3.6 g of copolymer was obtained. The polymerization rate was 15.1 g copolymer/g palladium.hour.

20 Example 3

A carbon monoxide/cyclopentene copolymer was prepared as follows. A stirred autoclave with a capacity of 250 ml was charged with 30 ml of cyclopentene and 30 ml of methanol. Herein was
25 dissolved a catalyst composition which comprised 0.1 mmol palladium acetate,
0.1 mmol para-toluenesulphonic acid,
3,0 mmol 2,2'-bipyridine, and
27.5 mmol 2,4-dinitrotoluene.

30 After air present in the autoclave had been removed by evacuation, 40 bar carbon monoxide was blown in. Then, the contents of the autoclave were heated to 70 °C. After 5 hours, polymerization was terminated by cooling to room temperature and releasing the pressure.

The reaction mixture was worked up as described in Example 1.

15 g of copolymer was obtained. The polymerization rate was 300 g copolymer/g palladium.hour.

5 Example 4

A carbon monoxide/cyclopentene copolymer was prepared substantially in the same way as in Example 3, the difference being that the catalyst composition comprised 3.0 mmol of 1,2-bis(ethylthio) ethane instead of 1,2'-bipyridine.

10 9.5 g of copolymer was obtained. The polymerization rate was 190 g copolymer/g palladium.hour.

Example 5

15 A carbon monoxide/cyclopentene copolymer was prepared substantially in the same way as in Example 3, except for the following differences

- a) the catalyst composition comprised 0.15 mmol of 1,3-bis(diphenylphosphino)propane instead of 2,2'-bipyridine, and
- 20 b) the reaction temperature was 80 °C instead of 70 °C.

5 g of copolymer was obtained. The polymerization rate was 100 g copolymer/g palladium.hour.

25 Example 6

A carbon monoxide/cyclopentene copolymer was prepared substantially in the same way as in Example 3, except for the following differences

- a) the catalyst composition comprised 30 mmol of 1,3-dinitrobenzene instead of 2,4-dinitro toluene, and
- 30 b) the reaction temperature was 80 °C instead of 70 °C.

14 g of copolymer was obtained. The polymerization rate was 280 g copolymer/g palladium.hour.

Example 7

A carbon monoxide/cyclopentene copolymer was prepared substantially in the same way as in Example 3, except for the following differences

- 5 a) the catalyst composition comprised 30 mmol of 2,6-dinitro toluene instead of 2,4-dinitrotoluene, and
b) the reaction temperature was 80 °C instead of 70 °C.

10 2.5 g of copolymer was obtained. The polymerization rate was 50 g copolymer/g palladium.hour.

Example 8

Example 3 was substantially repeated, except for the following differences

- 15 a) the catalyst composition comprised 40 mmol of 1,4-benzoquinone instead of 2,4-dinitrotoluene, and
b) the reaction temperature was 80 °C instead of 70 °C.
20

No polymer was formed.

Example 9

Example 3 was substantially repeated, except for the following differences

- 25 a) the catalyst composition comprised 40 mmol of nitrobenzene instead of 2,4-dinitrotoluene, and
b) the reaction temperature was 60 °C instead of 70 °C.

No polymer was formed.

30 Example 10

Example 3 was substantially repeated, except for the following differences

- a) the catalyst composition comprised 40 mmol of para-chloronitrobenzene instead of
35 2,4-dinitrotoluene, and

- b) the reaction temperature was 60 °C instead of 70 °C.

No polymer was formed.

Example 11

- 5 Example 3 was substantially repeated, except for the following differences

- a) the catalyst composition comprised 30 mmol of 1,2-dinitrobenzene instead of 2,4-dinitrotoluene, and

- 10 b) the reaction temperature was 80 °C instead of 70 °C.

No polymer was formed.

Example 12

- 15 Example 3 was substantially repeated, except for the following differences

- a) the catalyst composition comprised 3 mmol of 1,2-bis(ethylthio)ethane instead of 2,2'-bipyridine, and 40 mmol of 1,4-benzoquinone instead of 2,4-dinitrotoluene, and

- 20 b) the reaction temperature was 60 °C instead of 70 °C.

No polymer was formed.

Example 13

- 25 Example 3 was substantially repeated, except for the following differences

- a) the catalyst composition comprised 0.15 mmol of 1,3-bis(diphenylphosphino)propane instead of 2,2'-bipyridine, and 40 mmol of 1,4-benzoquinone instead of 2,4-dinitrotoluene, and

- 30 b) the reaction temperature was 60 °C instead of 70 °C.

No polymer was formed.

Example 14

Example 3 was substantially repeated, except for the following differences

- a) the catalyst composition comprised no
5 2,2'-bipyridine, and
- b) the reaction temperature was 80 °C instead of
70 °C.

No polymer was formed.

Of Examples 1-14, Examples 1-7 are examples in
10 accordance with the invention. In Examples 1 and 2, the
catalyst compositions employed contained a phosphorus
bidentate ligand chosen from group (1) as component c).
In Examples 3-7, the catalyst compositions employed
15 contained a bidentate ligand chosen from groups (2)-(4)
as component c) and in addition a meta-dinitrobenzene
compound as component d). With the aid of ^{13}C -NMR
analysis it was established that the copolymers
prepared according to Examples 1-7 had a linear
20 structure and that the units originating in carbon
monoxide and the units originating in cyclopentene
occurred in alternating order. Further, it was
established that the copolymers prepared according to
Examples 1 and 2 had a stereo-regular structure.
Finally, it was established with the aid of ^{13}C -NMR
25 analysis that in the copolymers prepared according to
Examples 1-7 at least 90% of the units originating in
cyclopentene were linked to both adjacent units
originating in carbon monoxide via their 1- and
3-carbon atoms. The copolymer prepared according to
30 Example 1 displayed a melting range of from 130 to
180 °C. When heated for 1 hour in nitrogen at 320 °C,
this copolymer was seen to lose 2% in weight. In a
comparative experiment carried out under the same
conditions and employing a linear alternating carbon
35 monoxide/ethene copolymer, the loss in weight was 18%.

Examples 8-14 fall outside the scope of the invention and have been included in the patent application for comparison. Examples 8-13 demonstrate that the catalyst compositions containing a nitrogen, sulphur or tetraaryl phosphorus bidentate ligand have insufficient activity for the copolymerization of carbon monoxide with cyclopentene, despite the presence of such compounds as 1,4-benzoquinone, nitrobenzene, para-chloronitrobenzene and 1,2-dinitrobenzene, which have an activity-enhancing effect when the said catalyst compositions are employed in the copolymerization of carbon monoxide with an alpha-olefin.

The meta-dinitrobenzene compounds that are added to the catalyst compositions according to the invention contain two nitrogen atoms which are separated from one another by a bridge formed by three carbon atoms. Example 14 was included to demonstrate that the favourable effect of these compounds cannot be explained from their possible acting as bidentate ligands.

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英文专利申请范围修正本(80年10月)

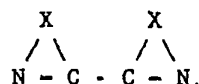
Chinese Patent Application No. 79101924

Amended Claims (October 1991)

1. Polymers of carbon monoxide with one or more mono-olefins, which polymers have a linear structure and in which polymers the units originating in carbon monoxide and the units originating in the applied olefins occur in alternating order, characterized in that the olefins used are one or more cyclopentenes, which are optionally substituted with one C_{1-4} alkyl group in either the 3, 4 or 5 position.
2. Polymers as claimed in claim 1, characterized in that they are copolymers of carbon monoxide with cyclopentene.
3. Polymers as claimed in claim 2, characterized in that they have a stereoregular structure.
4. Process for the preparation of polymers of carbon monoxide with one or more mono-olefins, which polymers have a linear structure and in which polymers the units originating in carbon monoxide and the units originating in the applied olefins occur in alternating order, which process comprises contacting the monomers in a diluent, at a temperature of 20-120 °C, an overall pressure of 5-150 bar, and a molar ratio of the olefin(s) relative to carbon monoxide in the mixture to be polymerised of 10:1 to 1:10, with such a quantity of a solution of a catalyst composition based upon
 - a) a palladium compound,
 - b) an anion of an acid with a pKa of less than 2, and
 - c) either
 - (1) a phosphorus bidentate ligand of the general formula $(R^3)_2P-R-P(R^3)_2$, wherein R^3 is an optionally polar-substituted aliphatic hydrocarbyl group of no more than 10 carbon atoms, and R is a bivalent bridging group having at least two carbon atoms in the bridge, or
 - (2) a phosphorus bidentate ligand of the general formula $(R^1)_2P-R-P(R^1)_2$, wherein R^1 is an optionally

polar-substituted aromatic hydrocarbyl group of no more than 10 carbon atoms, or

- (3) a sulphur bidentate ligand of the general formula $R^2S-R-SR^2$, wherein R^2 is an optionally polar-substituted hydrocarbyl group of no more than 10 carbon atoms, or
- (4) a nitrogen bidentate ligand of the general formula



wherein X is an organic bridging group containing three or four atoms in the bridge, at least two of which are carbon atoms,

as to contain 10^{-7} - 10^{-3} mol of palladium per mol of olefin to be polymerised,

characterized in that as olefins are used one or more cyclopentenes, which are optionally substituted with one C_{1-4} alkyl group in either the 3, 4 or 5 position, with the proviso that if a bidentate ligand chosen from the groups (2)-(4) is used as component c), the catalyst composition in addition includes a component d), which is a compound containing a benzene ring substituted with at least two nitro groups in a mutual meta position.

5. Process as claimed in claim 4, characterized in that a catalyst composition is employed which includes as component c) a phosphorus bidentate ligand in which R^3 is an alkyl group or in which R^1 is a phenyl group which is optionally substituted in a position ortho to the phosphorus atom with an alkoxy group, such as an ortho-methoxyphenyl group.

6. Process as claimed in claim 5, characterized in that a catalyst composition is employed which includes a phosphorus bidentate ligand in which the bridging group R has three atoms in the bridge at least two of which are carbon atoms, as component c).

7. Process as claimed in claim 4, characterized in that a catalyst composition is employed which includes a sulphur bidentate in which the bridging group R has only two carbon atoms in the bridge, such as 1,2-bis(ethylthio)ethane, as component c).

8. Process as claimed in claim 4, characterized in that a catalyst composition is employed which includes 2,2'-bipyridine or 1,10-phenanthroline as component c).

9. Process as claimed in claim 4, characterized in that a catalyst composition is employed which includes a phosphorus, sulphur or nitrogen bidentate ligand chosen from the groups (2)-(4) as component c) and a compound chosen from 1,3-dinitrobenzene, 2,4-dinitrotoluene and 2,6-dinitrotoluene as component d).

10. Process as claimed in claim 4, 5 or 6, characterized in that a catalyst composition is employed which includes a phosphorus bidentate ligand chosen from group (1) as component c) and 1,4-benzoquinone or 1,4-naphthoquinone as component d).